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COMPUTER TECHNIQUE for simulating the COMBUSTION OF CELLULOSE and other fuels

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Abstract: A computer method has been developed for simulating the combustion of wood and other cellulosic fuels. The products of combustion are used as input for a convection model that simulates real fires. The method allows the chemical process to proceed to equilibrium and then examines the effects of mass addition and repartitioning on the fluid mechanics of the convection column in a fire.

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Work on modeling a convective fire has been hampered until recently by the lack of a method to partition products of cellulosic combustion. Such a method is needed to develop data for input in a computer simulation of a real fire. We have now developed such a technique. It can simulate the combustion of wood and other fuels composed of the carbon, hydrogen, nitrogen, and oxygen atoms. The products computed can be used to specify the average molecular weight of gases injected into the lower boundary of a convection model and then transported into the convection column. The computer solves the governing differential equations of mass, energy, and momentum conservation. The amount of water vapor, carbon dioxide, and other gases produced by a fire is large enough to make the molecular weight of the convection column significantly different from that of the ambient air. The method developed can account for this difference. It allows the chemical process to proceed to equilibrium and then examines the effect of mass addition and repartitioning on the fluid mechanics of a convection column.

This note describes the analysis and simulation technique, and shows how the input requirements for a convective model can be specified. The following supplements to this note are available upon request to the Director, Pacific Southwest Forest and Range Experiment Station, P. O. Box 245, Berkeley, California. 94701. Attention: Computer Services Librarian:

- Instructions for using the computer programs.
- Computations of the equilibrium composition of end products of wood and other fuels for specified stoichiometric conditions.

CHEMICAL EQUILIBRIUM

The equilibrium states represent a limiting condition, and for any considerations of chemical reactivity, the equilibrium solution must first be known. In

high-temperature combustion processes, the kinetics of important reactions are fast. Consequently, the criteria as set forth by the van't Hoff reaction isocore, Gibbs-Helmholtz equations, Hamilton's principle, and statistical mechanics apply. Chemical thermodynamics require that for a specified system in equilibrium there is a unique composition. Any departures from equilibrium at high temperature represents a perturbation of the equilibrium states. Therefore, it is necessary to obtain the appropriate equilibrium solution before studying the non-equilibrium perturbations. The equilibrium state is specified from knowledge of the atomic composition along with the specification of any two state variables or thermodynamic properties.

This approach has been used successfully in the analysis and performance of liquid and solid rocket propellants[1]; evaluation of explosives[2]; and to develop techniques for measuring high temperature, pressure, and the kinetics of complex chemical reactions.[3] It has also been successfully applied to photolytic and atmospheric processes, and to the development of materials for solid state electronics systems.

ANALYSIS

The thermochemical data in our analysis were derived from the Joint Army-Navy-Air Force thermochemical tables.[4] And thermochemical data for the more complex species, such as the aromatic hydrocarbons and their derivatives, were taken from the American Petroleum Institute thermochemical tables.[5] The standard state was taken as 298.16°K. and 1 atmosphere pressure. ΔH_{298} for all species was arbitrarily taken as zero. The computer searches both sets of data and selects all species which are likely reaction products in a given system.

The composition of the major species was determined theoretically by solving the approximate mass-action equations or minimizing the free energy of the system subject to the constraint of atom conservation.[6] The chemical reactions can be expressed as:

$$\sum_{i=1}^{n} \nu'_{ij} X_{ij} \rightleftharpoons \sum_{i=1}^{n} \nu''_{ij} X_{ij}$$

The mass-action expression for the j'th reaction of this set is shown in Equation 2:

$$K_{pj} = \prod_{i=1}^{n} (P_{ij})^{(\nu''_{ij} - \nu'_{ij})}$$

A set of linear equations was derived by taking the logarithm of the mass actions expressions for each of the n reactions of Equation 2, expanding the resulting functions in a Taylor series, and rejecting all non-linear terms. The resulting set of equations is:

$$F(X) = \sum_{i=1}^{n} [X_i^g (C_i^g + 1n\, X_i^g / \bar{X})] + \sum_{k=1}^{q} X_k^c C_k^c$$

in which F(X) is the total free energy change in the system, X_i^g is the mole free energies for the i'th gaseous species, X_k^c is the mole free energy of the k'th condensed species, and C_i^g and C_k^c are the compositions of the i'th and k'th chemical species at equilibrium.

The set of linear equations was solved by the computer by using an iterative technique. To obtain a unique solution, it was necessary to impose the constraint of atom conservation:

$$\sum_{i=1}^{n} a_{ij} X_i^g + \sum_{k=1}^{q} a_{kj} X_k^c = bj \quad (j=1,2,\ldots,m)$$

in which a_{ij} is the number of atoms in the gaseous species, and a_{kj}, is the number of atoms of condensed species.

USE OR APPROACH

The success of this approach depends on the extent to which equilibrium is achieved; the inclusion of all important chemical species; the correctness of the thermochemical data; the validity of linearizing the mass action equations, and solving the resulting linear set; and the capability of the computing facility, i.e., the ability to maintain precision in calculations wherein successive operations are performed on extremely large and small numbers.

One way to assess the extent to which these five criteria are valid is to compare the test results with a computed solution. For many rocket performance studies,[1,2,8] the agreement between experiment and theory has been excellent.

This approach has proved useful in simulating the combustion of cellulose and other fuels, but realistic experiments would be necessary to determine the extent to which simulation results are valid.

For the fuel corresponding to wood, the composition expressed as weight fraction was:

$C_6H_{10}O_5$ (alpha cellulose)	0.54
$C_5H_8O_4$ (hemicellulose [pentosan])	.24
$C_{20}H_{21}O_6$ (lignin)	.20
Sodium (arbitrarily added)	.01
Potassium (arbitrarily added)	.01

We found that combustion in the presence of less than the stoichiometric amount of oxidizer produces

significant equilibrium concentrations of intermediate products or pollutants or both. These observations apply to the entire range of temperature and pressure investigated, and to each fuel system.

COMPUTER PROGRAM

The computer program we developed is an adaptation of two other programs for calculating the chemical equilibrium composition written by Gordon and McBride.[7] These are called CECS and ODE. In most versions available, CECS is written in Fortran IV for operation on the IBM 7090 computer.[8] We have adapted a version called the CESC70[7] to the IBM 360 computer.

The CECS70 version consists of a main program and 19 subroutines. One is a dummy subroutine (possibly a provision for a subroutine yet to be written) and six are used only for calculation of theoretical rocket performance–they may be replaced with dummy subroutines to speed compilation time. We have found that compilation time can be considerable, as the program fills about 3,000 punchcards.

NOTES

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